RAMAN SPECTRA OF CH_2Cl_2, $CHCl_3$ AND CCl_4 AT 64°K

P. K. BISHUI, D. K. MUKHERJEE AND S. C. SIRKAR

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32

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(PLATE 6)

ABSTRACT. The Raman spectra of crystals of methylene chloride, chloroform and carbon tetrachloride at 64°K have been investigated using liquid nitrogen boiling under reduced pressure as the refrigerant and in the case of chloroform the spectrum of the crystal at −120°C has also been investigated. A comparison has been made of these spectra with those for the crystals at 93°K. In the case of methylene chloride the changes undergone by some of the Raman frequencies with the lowering of temperature to 64°K indicate slight increase in the Cl–C–Cl angle and also formation of intermolecular H. . Cl. bond. In the case of chloroform the changes indicate transformation of the phase of the crystals in the range −120°C— −180°C and also formation of similar H . . Cl bond. In the case of carbon tetrachloride no appreciable change takes place in the Raman frequencies, but each of the lines 760 and 789 cm^{-1} seems to be sharper and to have a doublet structure at 64°K.

INTRODUCTION

The Raman spectra of chloroform and carbon tetrachloride in the solid state at about −180°C were investigated long ago by Sirkar (1936) and it was observed that some of the frequencies of chloroform undergo changes with the change of state while those of carbon tetrachloride remain unaltered. He also observed two low-frequency lines in the spectrum of solid chloroform and one such line at 85 cm^{-1} in the case of carbon tetrachoride at about −180°C. Subsequently, the Raman spectra of a large number of aromatic compounds in the frozen state at different low temperatures were studied by several workers (Ray, 1950, 1952; Biswas, 1954, 1955 and others) and some changes in the positions of the low-frequency lines with the change of temperature of the crystals were observed. More recently Sirkar *et al.* (1964) studied the Raman spectra of frozen benzene and carbon disulphide at −209°C and observed slight shifts of some of the low-frequency lines from their positions at -180°C. The lines were attributed to angular oscillations of the molecules in the crystals, the restoring forces being provided by intermolecular hydrogen bond-formation in the case of benzene and to formation of polymeric chains by the molecules in the case of crystals of carbon disulphide. Ito (1964) also studied the spectra of chloromethanes at 77°K. The behaviour of simple molecules of substituted methanes in the solid state at as low a temperature at −209°C was not known and, therefore, it was thought worthwhile to study the Raman spectra of methylene chloride, chloroform and carbon tetrachloride at −209°C in order to find out the nature of intermolecular forces acting in these crystals at such low temperatures.

EXPERIMENTAL

The experimental arrangement used earlier by Sirkar *et al.* (1964) was used in the present investigation also. Liquid nitrogen boiling under reduced pressure was used as the refrigerant to obtain a bath at −209°C. The liquids used were of chemically pure quality and they were redistilled under reduced pressure. Kodak 127 panchromatic films were used to photograph the spectra. In order to detect small changes in the positions of the Raman lines care was taken to photograph the comparison spectrum of iron arc without any lateral shift which could be detected by comparing the relative positions of the 4916A line of mercury and the 4919A line in the iron arc spectrum. The Raman spectra of the substances in the liquid state and in the solid state at −180°C were also photographed with the same spectrograph on other portions of the same roll of film in order to find out whether there was any change in the relative intensities of the lines. In the case of chloroform the Raman spectrum of the crystals at about −120°C was also photographed.

RESULTS AND DISCUSSION

The Raman lines observed are given in Tables I, II and III and some of the spectra are reproduced in Figures 1, 2 and 3, (Plate 6). The results are discussed separately for the three substances in the following sections.

Methylene chloride

The Raman spectrum of this compound at −160°C was studied previously by Mazumder (1949). He observed slight changes in the Raman frequencies. The frequencies 287 and 1158 cm^{-1} were found to increase to 293 and 1164 cm^{-1} respectively while the lines at 706, 737, 1424 and 2988 cm^{-1} were found to shift to 702, 730, 1413 and 2983 cm^{-1} respectively. Table I shows that at −180°C a new line 94 cm^{-1} is observed and except the line 745 cm^{-1} all the other lines have almost the same frequency-shifts as at −160°C. It appears that with the appearance of the new line at −180°C the line 737 cm^{-1} of the molecule in the liquid state splits up into two lines at 730 and 745 cm^{-1} respectively. When the temperature of the crystals is reduced further to −209°C the line 294 cm^{-1} appears to be broad, but on closer examination it is found to consist of two sharp components at 291 and 296 cm^{-1} respectively. Further, the frequency-shifts 745 and 1165 cm^{-1} increase respectively to 748 and 1168 cm^{-1} while the line 1415 cm^{-1} does not shift any further. Ito (1964) also observed the splitting of the line 737 cm^{-1} in the case of the crystals at 77°K, but the splitting of the line 1158 cm^{-1} observed by him is not confirmed in the present investigation.

The assignment of the lines due to the CH_2Cl_2 molecule was fully discussed by Herzberg (1945). The lines 287, 706 and 737 cm^{-1} are due respectively to C-Cl deformation and to symmetric and asymmetric C-Cl stretching vibrations.

The slight diminution of the frequencies of the symmetric stretching vibration and increase in the frequencies of both deformation and asymmetric stretching

TABLE I

Methylene chloride

$\Delta\nu$ in cm^{-1}

Liquid	Solid		
	−160°C (Mazumder, 1949)	−180°C	−209°C
		94 (1b)	94 (1b)
287 (8)	293 (3)	294 (2)	291 (0)
			296 (1)
706 (10)	702 (5)	700 (5)	700 (5)
		730 (0)	735 (0)
737 (2)	730 (0)	745 (1)	748 (1)
1158 (1b)	1164 (1)	1165 (0)	1168 (0)
1420 (3)	1413 (2)	1415 (2)	1415 (2)
2988 (10)	2983 (5)	2983 (5)	2983 (5)
3056 (2)	3058 (2)	3056 (1)	3056 (1)

vibrations indicate that most probably the Cl-C-Cl angle increases a little in the solid state at −180°C. The Raman line 1158 cm^{-1} has been assigned to the torsional oscillation and increase in this frequency with solidification indicates probably the formation of weak Cl. .H bond in the solid state. The fact that the frequency further increases to 1168 cm^{-1} at 64°K corroborates this conclusion, because such a bond becomes stronger with the contraction of the crystals at the lower temperature.

As regards the C-H oscillations, the line 1424 cm^{-1} which has been assigned to the deformation oscillation shifts to 1415 cm^{-1} in the spectrum due to the crystals at −180°C and remains almost in the same position upto 64°K. The lines 2988 cm^{-1} and 3056 cm^{-1} due to C-H stretching oscillations do not shift appreciably with the lowering of temperature of the crystals. The change in the latter two frequencies with solidification of the liquid is also negligible. Hence it appears that the H-C-H angle does not change appreciably with the solidification of the liquid. The slight lowering of the frequencies of symmetric deformation and stretching oscillations may be due to slight weakening of the C-H bond. These facts together with the increase in the frequency of torsional oscillation probably indicate that weak intermolecular H . . Cl bonds are formed in a direction perpendicular to the H-C-H plane.

The new line 94 cm^{-1} is sharper at −180°C than at −209°C. The line 294 cm^{-1} also splits up into two lines at the lower temperature. These changes may be attributed to the asymmetry of the intermolecular forces in the unit cell at 64°K.

Chloroform

Table II shows that when the liquid is solidified and cooled to about —120°C the line 3019 cm^{-1} due to C-H stretching oscillation shifts to 3008 cm^{-1} and the line 1216 cm^{-1} splits up into two lines at 1208 cm^{-1} and 1224 cm^{-1} and a new line at 95 cm^{-1} appears in the spectrum. The changes in the former two lines can be explained on the assumption that weak intermolecular H . . Cl bond is formed in the crystals at this temperature. When the temperature is lowered to—180°C a single line at 1232 cm^{-1} appears in place of the two lines mentioned above, the line 95 cm^{-1} splits up into two lines at 76 cm^{-1} and 97 cm^{-1} respectively

TABLE II

Chloroform

$\Delta\nu$ in cm^{-1}

Liquid	Solid		
	—120°C	—180°C	—209°C
		76 (1b)	78 (1)
	95 (2b)		
		97 (1)	98 (1)
261 (10)	261 (2b)	260 (1)	260 (2)
		274 (1)	274 (2)
365 (8)	367 (4)	368 (4)	
			371 (3)
668 (8)	670 (4)	672 (5)	676 (4)
761 (4b)	760 (2b)	752 (2)	752 (2)
		766 (0)	766 (0)
	1208 (0)		
1216 (1)			
	1224 (0)	1232 (1)	1234 (1)
3019 (3)	3008 (4)	3016 (5)	3014 (5)

and the line 3008 cm^{-1} shifts to 3016 cm^{-1}. This latter spectrum at —180°C was discussed by one of the authors (Sirkar, 1936) long ago. The results of the present investigation, however, show that probably a change of phase of the crystal takes place when the temperature is lowered from —120°C to —180°C, because the frequency 3008 cm^{-1}, instead of diminishing slightly, increases while the two lines 1208 cm^{-1} and 1224 cm^{-1} are replaced by a line of higher frequency-shift at the lower temperature. The line 1204 cm^{-1} observed by Ito (1964) in the case of the crystals at 77°K is not observed in the spectra of the crystals either at —180°C or at —209°C in the present investigation. By studying the infrared spectra of crystals of chloroform at the temperatures 80°K and 150°K, Denaricz (1965) also came to such a conclusion. She observed two bands at 1203 cm^{-1} and 1223 cm^{-1} in the spectrum of the crystals at 150°K and almost an unresolved doublet at 1219.7 cm^{-1} and 1222.2 cm^{-1} in the spectrum of the crystals at 80°K. In the Raman spectrum in the latter case the frequency-shift of the single line observed is, however, 1232 cm^{-1} and not 1221 cm^{-1} observed by her as the mean frequency. When the temperature of the crystal is lowered to 64°K no remarkable

change takes place in the spectrum, but small changes take place in some of the frequencies. The lines 672 cm^{-1}, 1232 cm^{-1} and 3016 cm^{-1} shift respectively to 676 cm^{-1}, 1234 cm^{-1} and 3014 cm^{-1}. Changes in the latter two frequencies indicate slight increase in the strength of the intermolecular H . . Cl bond in the crystal. The frequencies 76 and 97 cm^{-1} also increase respectively to 78 and 98 cm^{-1} at 64°K for the same reason. These two frequencies are to be attributed to angular oscillations of the molecule about the two-fold axes of the tetrahedron to which the structure of the molecule would approximate if the hydrogen atom were assumed to be replaced by a chlorine atom.

Carbon tetrachloride

The Raman spectrum of carbon tetrachloride at —183°C was first investigated by one of the authors (Sirkar, 1936) and it was observed that the frequencies of the molecule do not undergo any change with the change of state and lowering of temperature, but a new line appears at 85 cm^{-1}. The Raman spectrum of this substance at 200°K was studied later by Morino *et al.* (1942) who did not observe any new low-frequency line but observed the line 789 cm^{-1} to be split up into two lines at 780.2 and 792.4 cm^{-1} respectively. Recently, the Raman spectrum of the substance at 77°K has been studied by Ito (1965) using a high resolution spectrograph and he has observed the lines 760 cm^{-1} and 789 cm^{-1} to be split up into four lines at 758.2, 767.5, 782.0 and 793.6 cm^{-1} respectively. Although in a note

TABLE III

Carbon tetrachloride

$\Delta\nu$ in cm^{-1}

Liquid	Solid		
	93°K	77°K (Ito, 1965)	64°K
	88 (1b)		96 (2b)
219 (5)	219 (3)	219.7 (s)	219 (3)
314 (5)	314 (4)	313.5 (w)	314 (4)
		317.1 (s)	
459 (6)	459 (5)	456.7 (m)	459 (5)
		460.2 (vs,sh)	
		463.1 (vs,sh)	
760 (2b)	760 (1,sh)	758.2 (m)	758 (1)
		767.5 (w)	765 (0)
789 (2b)	789 (1,sh)	782.0 (w)	784 (1)
		793.6 (m)	792 (0)

published earlier (Ito, 1964) he reported a new line at 99 cm^{-1}, in the later paper this line was absent. The spectrum of the crystals at 93°K was again photographed besides that at 64°K in order to find out whether the splitting of the lines 760 cm^{-1} and 789 cm^{-1} takes place at these temperatures. A careful comparison of the spectra of the compound in the liquid state and in the solid state

at 93°K and 64°K shows that the width of each of the lines 760 cm^{-1} and 789 cm^{-1} of the liquid is about 12 cm^{-1}, but in the spectrum of the solid at 93°K this width is about 5 cm^{-1}, while at 64°K each of the lines becomes broader and seems to consist of two components touching each other as shown in Table III. The region between 760 cm^{-1} and 789 cm^{-1} in the spectrum due to the crystals at 93°K is a little darker than the general background, but as these two lines are weak the two weaker components observed by Ito (1965) are not observed in the present investigation. It appears that already in the liquid state each of these two lines has an unresolved structure and at 64°K, as the components become sharper, each line appears as a close doublet.

As regards the low-frequency region of the spectrum a broad line at 88 cm^{-1} appears in the spectrum of the crystal at 93°K and the line shifts to 89 cm^{-1} when the temperature is lowered to 64°K. With the spectrograph used in the present investigation the splitting observed by Ito (1965) of the lines 314 cm^{-1} and 459 cm^{-1} could not be observed and the total width of each of these lines in the spectrum was found to be about 5 cm^{-1}.

It appears from the results discussed above that formation of hydrogen bond is mainly responsible for the small changes of the lines of these chlorine substituted methanes in the solid state observed in the present investigation, because in the case of carbon tetrachloride no appreciable change in the vibration frequencies takes place with solidification of the liquid and lowering of temperature upto 64°K.

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